

Chemical Oceanography of the Arabian Sea: Part III — Studies on Nutrient Fraction & Stoichiometric Relationships in the Northern & the Eastern Basins

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Phosphorus and inorganic nitrogen compounds have been divided into 'reserved' and oxidative fractions based on their relationships with apparent oxygen utilization in the northern and the north-eastern basins of the Arabian Sea. Two oxygen minima are observed in the water masses north of 20°N latitude. The reserved nitrogen compound is negative in the deeper waters and this varies from north to south. This deficit indicates a possible loss of nitrate to gaseous nitrogen through denitrification. Spatial variation of oxidative ratios indicates changes in the rates of nutrient regeneration associated mainly with regional variations in photosynthetic productivity. A stoichiometric relationship based on the ratios of change of nutrients in water and their ratios of concentration in plankton indicates that organisms in the Arabian Sea may have an atomic relation for C:N:P of 105:15:1. Applying the oxidative ratios the loss of nitrate through denitrification has been calculated to be about 2/3 of its total availability. Similarity of conditions between this area and the eastern tropical North Pacific suggests denitrification as a characteristic on the eastern sides of oceans which are poorly ventilated in the north.

LARGE volume of chemical oceanographic data has been collected during the International Indian Ocean Expedition 1960-65. Literature records of studies on various chemical parameters in the Arabian Sea are now available¹⁻⁶. Almost all these studies are concerned with the distributive aspects of different chemical constituents. No analysis has so far been made on the quantitative relations between nutrients and oxygen. Similar studies have been carried out in other oceanic areas and semi-enclosed basins⁷⁻¹⁶. In this report an attempt has been made to examine approximate relationships between phosphorus, inorganic nitrogen compounds and dissolved oxygen based on the data collected on board *INS Darshak* during its cruises (1973-74) to the northern and north-eastern basins of the Arabian Sea (Fig. 1). These relationships can be usefully applied to calculate the rate of oxygen consumption by organic material during their decomposition in studies of coastal pollution and in areas with poor water exchange.

Materials and Methods

Salinity, temperature, dissolved oxygen, inorganic phosphate, total phosphorus, nitrate-nitrogen, nitrite-nitrogen, ammonia-nitrogen, pH and total alkalinity were measured for water samples collected from standard depths from hydrographic casts using transparent TPN water samplers (type Hydro Bios, Kiel, West Germany). All the analyses, except total phosphorus, were carried out on board immediately after the collection of samples following standard methods¹⁷⁻²⁵.

Plankton — Plankton samples were collected and analysed by a procedure described by Sen Gupta and Koroleff¹⁶. In the beginning nitrogen was

analysed applying the micro-kjeldahl technique, but when chemicals of required purity were available it was estimated by the same method as described in the reference.

The samples were analysed by different analysts on board and in the laboratory and as such errors, due to personal bias, in them cannot be uniform.

Hydrographic Features

The Arabian Sea, exclusive of the Gulfs of Aden and Oman, occupies an area of about 7.5×10^6 km² and forms the north-western part of the Indian Ocean. For the study of the oceanographic features, Schott²⁶ bounded the Arabian Sea as follows: "the southern boundary runs from the Indian coast near Goa, along the western side of the Laccadive islands to the equator; thence it trends slightly south to the point on the east African coast near Mombasa, at approximately 5°S latitude". The Arabian Sea is an area of negative water balance. Annual excess of evaporation over precipitation and runoff varies between 7 and 10 km³ with two maxima during the north-east and the south-west monsoons²⁷. Due to the influence of surrounding landmass the NE monsoon is quite weak in this area, while the SW monsoon is very intense with wind speeds reaching a maximum of 25-30 knot, causing strong upwelling along the coast of Somalia on its western side and a comparatively weaker upwelling along the Indian coast on its eastern side. The water mass in the Arabian Sea is regulated by the out-flowing high saline waters from the Persian Gulf through the 50 m deep sill at the Hormuz Strait and from the Red Sea through the 125 m deep sill at the Strait of Bab-el-Mandeb. Its water masses are composed of a high saline water at the

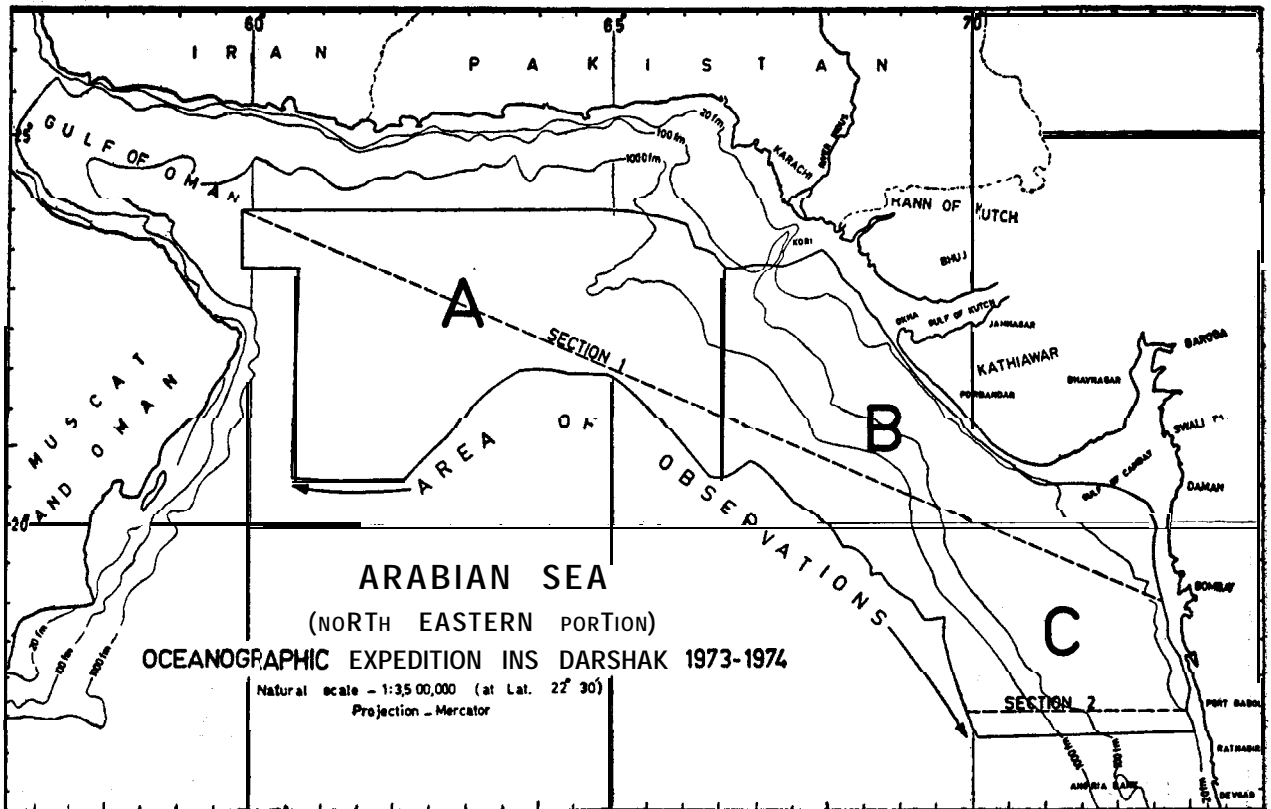


Fig. 1 -Area of observations in the Arabian Sea (north-eastern portion) during oceanographic expedition of INS Darshak (1973-74)

surface layers, called the Arabian Sea surface water, an intermediate layer consisting of both Persian Gulf and Red Sea waters, and deep and bottom waters originating in the equatorial region of the Indian Ocean and in the Antarctic circumpolar waters respectively¹.

Because of high temperature in the surface layers and low oxygen contents in the intermediate waters of the equatorial Indian Ocean the oxygen concentrations are comparatively lower in the Arabian Sea. There is always a minimum of oxygen at an intermediate depth and north of 18°N latitude 2 minima can be detected (Fig. 2).

To illustrate this point further, distribution of oxygen is shown along a transverse section in the NW-SE direction between 19°00'N and 24°00'N (section 1, Fig. 1) and another section normal to the coast along 17°30'N (section 2, Fig. 1). It can be seen from Fig. 3 that there are 2 oxygen minima, the first one between 350 and 600 m and the other between 850 and 1100 m, the depths of both of which increase southwards. Decrease in oxygen concentration at the first minimum layer also shows a southward intensification.

Fig. 4 almost confirms the above statements. The second oxygen minimum is absent and the depth of the oxygen minimum layer, with values lower than those in Fig. 3 and appearing almost at the shelf-break, extends from about 200 m to 1100 m.

We shall, however, make one reservation here. It has been observed¹⁴ that at concentrations below

25 µg-at/litre (~0.3 ml/litre) Winkler oxygen values are consistently high by 8-10 µg-at/litre (~0.1 ml/litre). Due to practical difficulties the colorimetric oxygen method could not be applied. Therefore, present low oxygen values might be slightly higher, but then, the accuracy of the Winkler method is no better than 0.05 ml/litre.

Two distinct features of the oxygen minimum zone are the apparent deficits in nitrate and the unusually high concentrations of nitrite. Nitrate is presumably absent in this layer as an intermediate product of the process leading to free nitrogen (denitrification). A secondary nitrite maximum has, also, been observed occasionally at the deeper oxygen minimum. Since nitrite concentrations are higher than those at the upper oxygen minimum with increasing nitrate concentrations, nitrite in this layer is suggested to be an intermediate product of the reverse process, i.e. nitrification²⁸.

Photosynthetic productivity in the Arabian Sea is higher than that in other oceanic areas²⁹⁻³¹. A high concentration of organic matter, resulting from high photosynthetic productivity at the surface, when gets accumulated deeper down, will deplete the oxygen concentration in that layer because of decay and degradation. This and also the sluggish water circulation at an intermediate depth may sometimes produce near-anoxic or sub-oxic conditions at that level, which, in the Arabian Sea, has been termed as an 'azoic zone'³². Vertical mixing processes from the oxygen-rich deep and bottom waters in the Arabian Sea do not appear

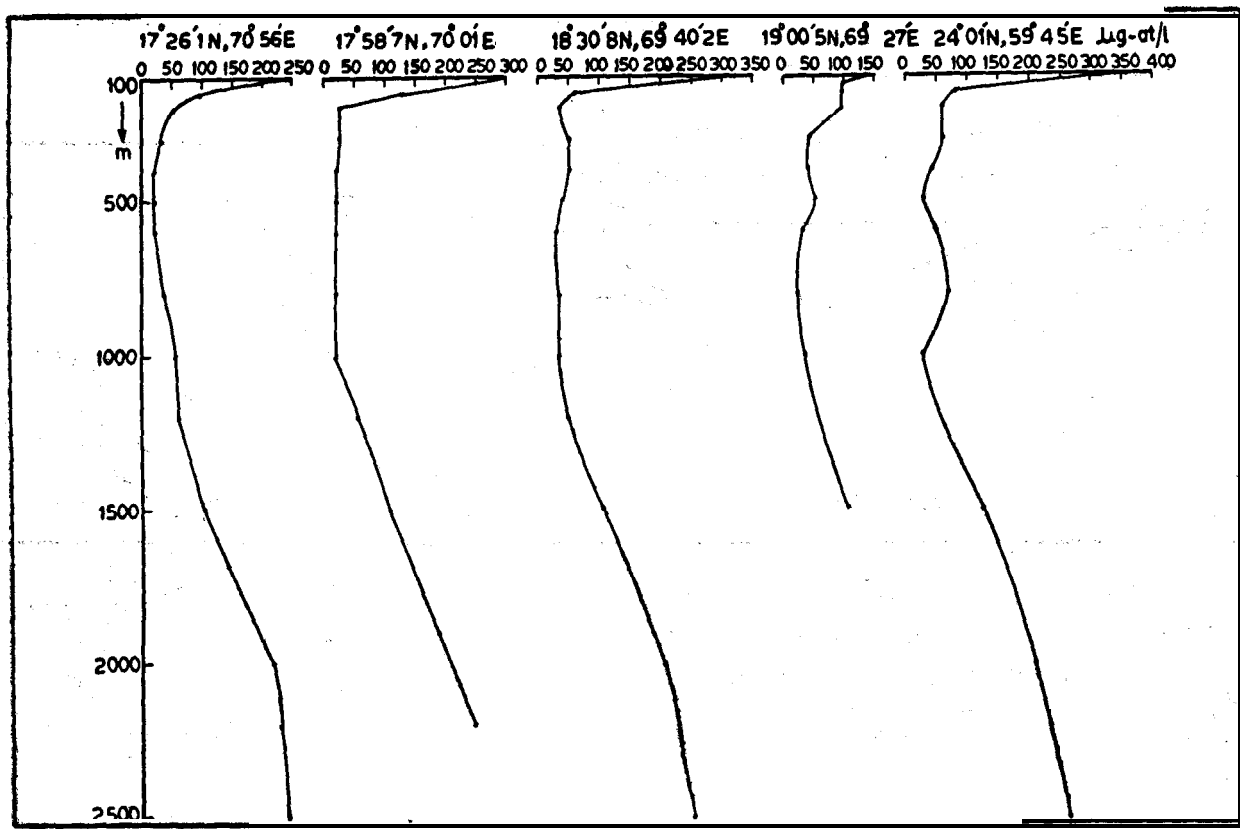


Fig. 2— Dissolved oxygen in $\mu\text{g-at/litre}$ versus depth-latitudinal variation

to be sufficiently strong to compensate for this deficiency in oxygen.

Results and Discussion

Nutrient Fractions in Relation to Oxygen Utilization

Phosphate (expressions phosphate, nitrate, nitrite and ammonia used in this paper stand for phosphate-phosphorus, nitrate-nitrogen, nitrite-nitrogen, and ammonia-nitrogen respectively) present in oxygen-saturated water at the surface, just before it starts sinking, has been termed as 'preformed phosphate' by Redfield³³. Because of practical difficulties in ascertaining 'preformed' phosphate in a water mass Sugiura³⁴ introduced the term 'reserved' which is the phosphate concentration obtained by subtracting phosphate of oxidative origin from the total inorganic phosphate. In this study we have used the term 'reserved' in the above sense.

Redfield *et al.*⁷ worked out the relationship between phosphorus, nitrogen and carbon on the basis of their concentrations in plankton. The atomic ratios in organisms, obtained by them, for carbon, nitrogen and phosphorus are 106:16:1. The relationship between oxygen consumption and carbon dioxide production as calculated by them is 276:106 by atoms. These relations are obtained from an examination of their composition in plankton, of water masses and theoretical considerations. The relationship in water obtained from the slope of the regression line between the nutrients

and the apparent oxygen utilization ($\text{AOU} = \text{O}'_2 - \text{O}_2$, where O_2 is the observed oxygen conc. and O'_2 is the conc. of dissolved oxygen in water, having the observed salinity and temperature when in equilibrium with a water-saturated atmosphere) gives almost the same ratios. Redfield *et al.*⁷ have concluded that concurrent changes in the concentrations of carbon, nitrogen and phosphorus in water would be almost equal to their ratios of concentration in plankton.

We have divided the water masses of the Arabian Sea chemically into 2 layers, an upper layer between the surface and 125 m and a lower layer from 125 m to the depths of the maximum AOU values. The upper layer, where photosynthetic productivity takes place, is well oxygenated down to the thermocline depth. At the thermal discontinuity layer there is always a sharp decrease in oxygen concentration and at about 125 m values as low as 0.2 ml/litre O_2 have often been observed. Therefore, it is apparent that oxidation processes start almost at or just below the thermocline and the respiration rates may reach a pretty high intensity almost immediately. The depth of the low-oxygenated layer stretches down to about 1000-1200 m. Possibility of advection of this oxygen; poor water upwards resulting in decrease in oxygen concentration cannot be ruled out also.

The lower layer has been selected following the accepted ideas about the oxidation of organic matter in the oceans^{7,8}. To start with we have pooled together values from all stations in the area

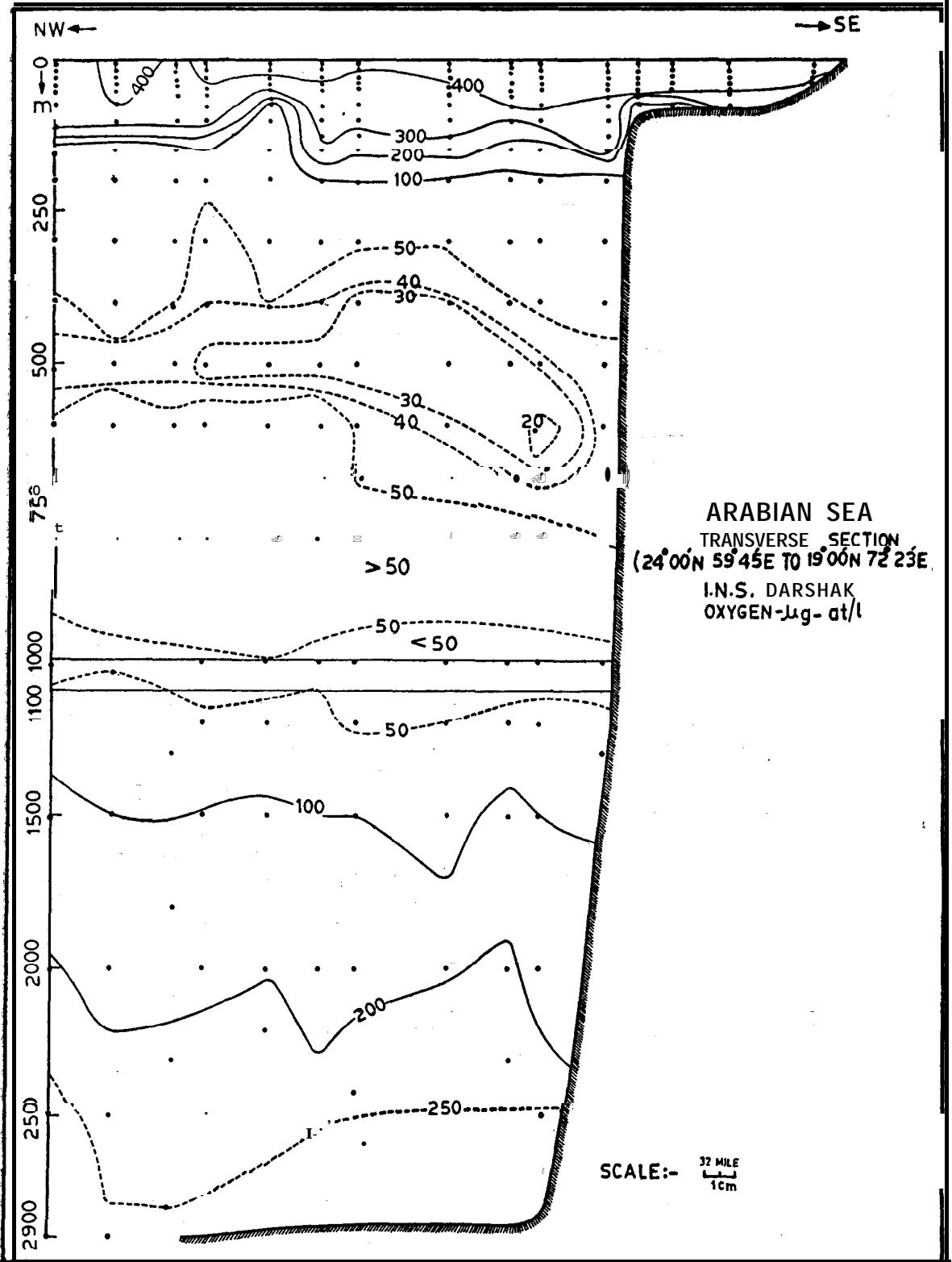


Fig. 3 — Distribution of oxygen across a transverse section in NEXSE direction (section 1, Fig. 1)

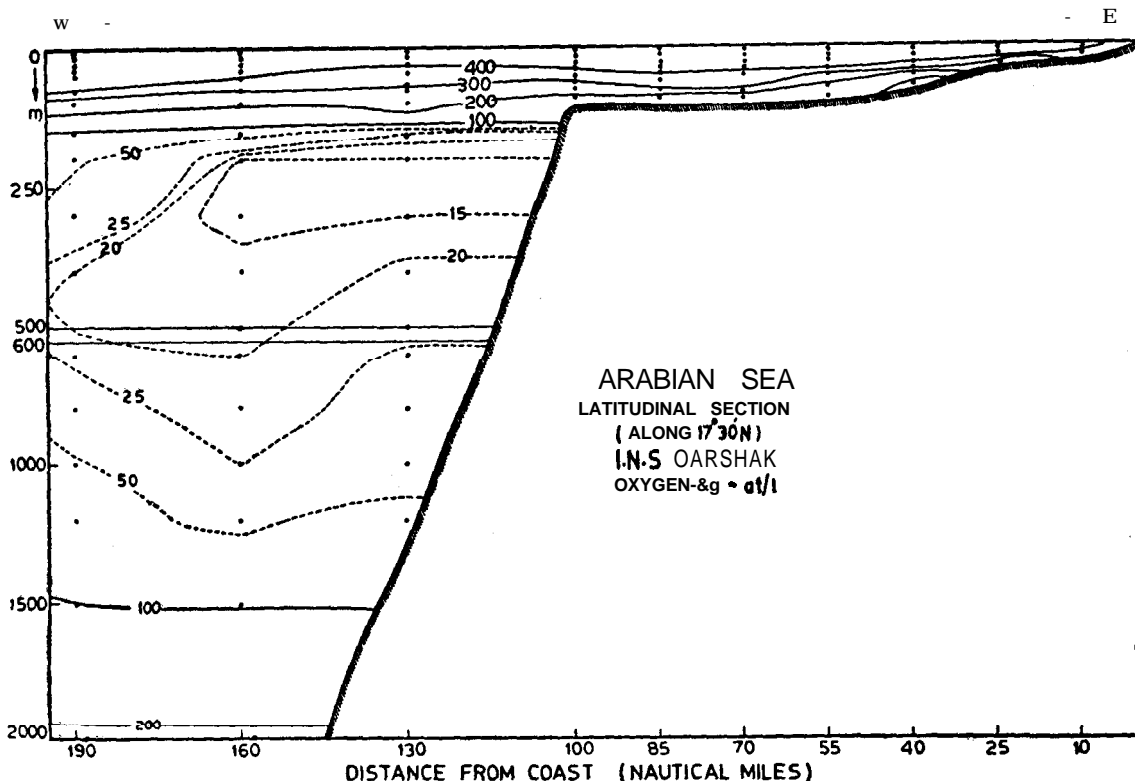


Fig. 4-Distribution of oxygen along 17°30'N latitude in an east-west section

of observation assuming that regional variations in the oxidation intensity may not be very significant from the viewpoint of totality.

Oxygen content in the surface waters of the area studied varies from 10% supersaturation to 10% undersaturation. This will cause errors in the AOU values (as calculated from the nomogram of Green and Carritt⁸⁵) but the errors are small compared to the variations of AOU. Sinking of surface waters in oceans usually takes place during the winter months resulting in somewhat supersaturation of oxygen in the upper few metres. But in the equatorial and the tropical regions of the oceans, where the winter is always very mild and where often evaporation exceeds precipitation and runoff, it is not yet clearly understood to what extent this may influence the sub-surface oxygen concentrations. However, in the present calculations those values of nutrients where the surface layers were calculated to be supersaturated with oxygen are omitted.

Fig. 5 shows the relationship between the apparent oxygen utilization and inorganic phosphate in the upper layer at all the stations. The slope of the regression line gives a ratio of 286:1 by atoms. The relation between nitrate and phosphate, calculated in the same way, gives an atomic relation of 6.4:1 between them (Fig. 6). Combining $\Delta\text{AOU}:\Delta\text{P}$ in Fig. 5 with AN:AP in Fig. 6 AAOU:AN as 45:1 by atoms is obtained.

In marine environment inorganic nitrogen compounds may exist in their oxidizing or reducing forms. The general cycle is $\text{NO}_3 \rightleftharpoons \text{NO}_2 \rightleftharpoons \text{NH}_3$. The occurrence and predominance of different forms

depend on the stage of the process. But phosphate occurs mostly as orthophosphate, the highest oxidation state of phosphorus compounds. Surplus phosphate together with the addition by advection from the deeper water will cause an excess of this component in the upper layer. Deficiency in oxygen will cause the nitrogen compounds to undergo reduction, in deep waters. Moreover, addition of nitrate by advection to this layer is not very significant due to its low concentrations in the layers just below. Thus it appears that the relation $\Delta\text{N}:\Delta\text{P}=6.4:1$ atoms is the result of the presence of excess phosphate and consequently $\Delta\text{AOU}:\Delta\text{N}=45:1$ atoms will not be representative of the actual nitrate produced during the respiration processes. Moreover, zero or near-zero values of AGU at or near the surface, caused by the atmospheric exchange, will also affect the ratio.

Fig. 7 shows the relationship between apparent oxygen utilization and inorganic phosphate at all stations from the deeper layers. The slope of the regression line gives a ratio of oxygen consumption to phosphate regeneration of 270:1 by atoms. From Fig. 8 we get AN:AP ratio in deep waters of 17:1 by atoms. Combination of these 2 ratios gives an atomic relation of 16:1 for AAOU:AN. For reasons mentioned above we decided to apply these relationships to examine the oxidation of organic matter in both the layers as, we believe, that would give a more realistic picture of the real state of affairs.

Following Sagi¹³ who introduced the concept 'reserved nitrate' in the same way as 'reserved phosphate' by Sugiura³⁴ in his observations in the

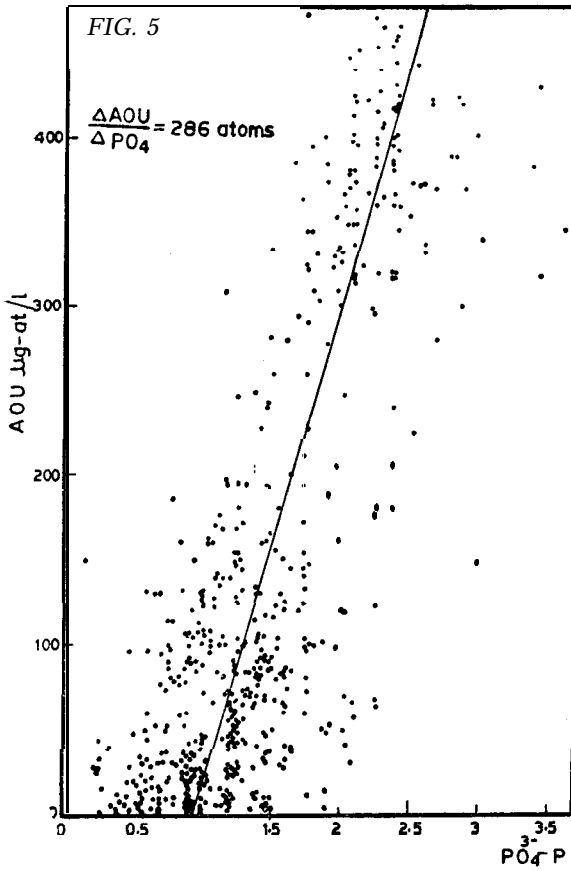


Fig. 5 — Correlation between phosphate-phosphorus and apparent oxygen utilization in the upper layers (0-125 m)

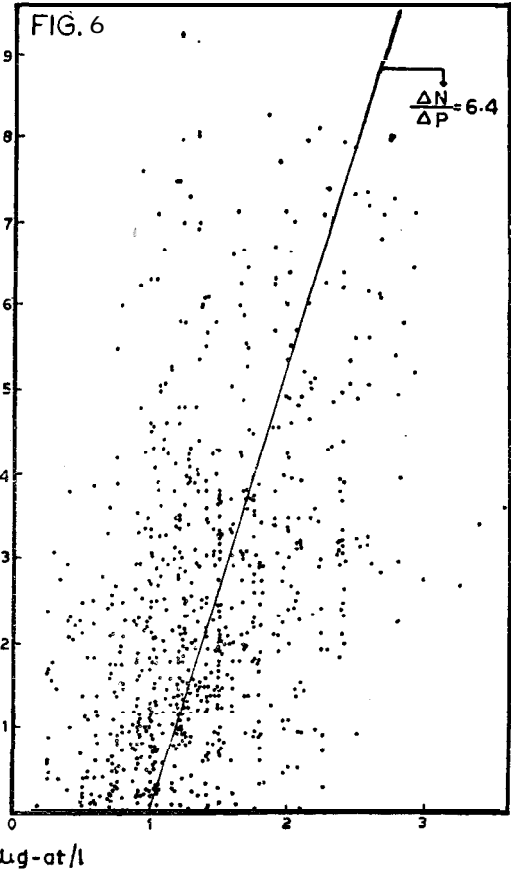


Fig. 6 — Correlation between nitrate-nitrogen and phosphate-phosphorus in the upper layers (0-125 m)

Pacific Ocean, Sen Gupta and Koroleff¹⁶ could study the deficit of nitrate and denitrification in the oxygen-poor waters of the Baltic Sea. The same analysis is applied here in an attempt to study nitrification and/or eventual denitrification in the oxygen-poor layers of the Arabian Sea. However, in the case of the nitrogen compounds nitrite and ammonia must be considered.

The total phosphorus and inorganic nitrogen compounds have been separated into their constituent fractions according to Redfield *et al.*⁷ and these are presented in Table 1.

To test constancy and validity of the $\Delta\text{AOU}:\Delta\text{P}$ ratio in the depth interval 150 m-AOU maximum reserved phosphate (P_r) was calculated from the relations outlined in Table 1 and plotted against salinity¹⁴, for all the stations (Fig. 9). The relation between potential temperature and salinity at this depth interval is linear. But Fig. 9 indicates three distinctly separate areas where individually P_r is approximately linear with salinity. Varying P_r values will result from different rates of mixing and slower or faster rates of oxidation of organic matter. Inorganic phosphate that can be liberated during nitrate reduction is estimated to be no greater than $0.17 \mu\text{g-at/litre}$, assuming that the ratio is $\Delta\text{NO}_3:\Delta\text{PO}_4=94.5$ (ref. 9) during denitrification and that on average $16 \mu\text{g-at/litre}$ of nitrate ion has been reduced. No attempt has been made to correct for this contribution to the phosphate pool.

TABLE 1 — DEFINITION OF VARIOUS FRACTIONS OF PHOSPHORUS AND NITROGEN

Fraction	Phosphorus	Nitrogen
Total	Analysis after oxidation (P_t)	Analysis after oxidation (Nt)
Inorganic	Direct analysis	Direct analysis for $\text{NO}_3^- + (\text{NO}_2^- + \text{NH}_3)$
Oxidative	$P_{ox} = \text{AOU}/270$	$\text{Nox} = \text{AOU}/16$
Reserved	$P_r = \text{PO}_4^{3-} - P_{ox}$	$N_r = \text{NO}_3^- - \text{Nox}$
Organic + particulate	$P_t - \text{PO}_4^{3-} - P$	Nt-(NO ₃ ⁻ + NO ₂ ⁻ + NH ₃)

Following the demarcations obtained in Fig. 9 the total area of observations was divided as (A) between $20^{\circ}00'$ and $24^{\circ}30'N$ west of $66^{\circ}30'E$ longitude; (B) between the same latitudes east of $66^{\circ}30'E$; and (C) between $17^{\circ}30'$ and $20^{\circ}00'N$ latitude normal to the Indian coast, and are marked in Fig. 1. Averages of values of all the variables considered have been calculated for the areas separately and are presented in Table 2.

Nutrients of oxidative origin are usually those fractions which have been regenerated in the water from the decomposition of organic and detrital material and which are directly proportional to the depletion of dissolved oxygen. The oxidative fraction can thus be calculated from the apparent oxygen utilization and the $\Delta\text{AOU}:\Delta\text{P}$ ratio.

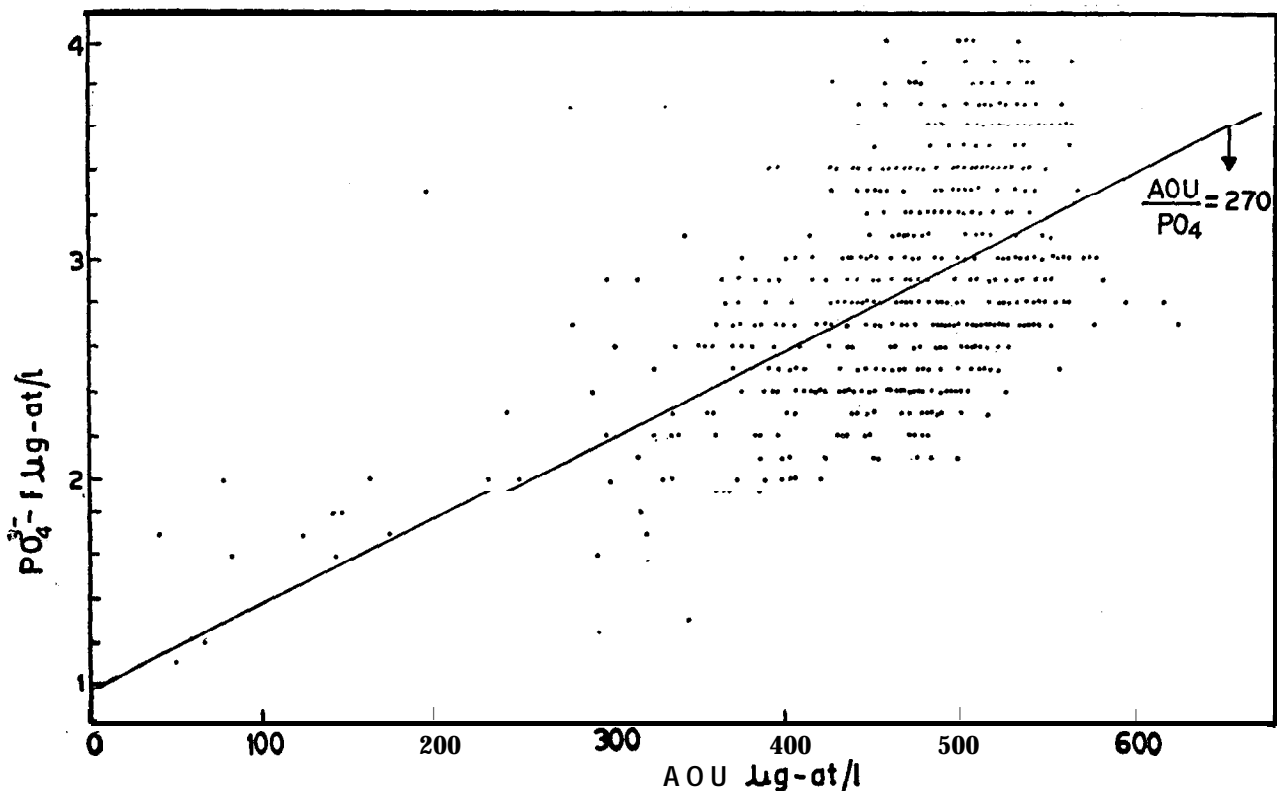


Fig. 7 — Correlation between phosphate-phosphorus and apparent oxygen utilization in the deeper layers (from 150 m to AOU maximum)

TABLE 2 — AVERAGE VALUES OF VARIABLES CONSIDERED

Parameter $\mu\text{g-at/litre}$	Area surface to 125 m	A' 125 to 900 m	Area surface to 125 m	B* 125 to 900 m	Area surface to 125 m	c* 12s to 900 m
$\text{PO}_4^3\text{-P}$	1.27	2.9	1.55	3.4	0.82	2.58
Total P	2.26	2.44	2.76	4.03	1.76	2.69
Organic P + particulate P	0.99 (45)†	0.54 (16)‡	1.21 (44)‡	0.63 (16)‡	0.94 (53)‡	0.11 (4)‡
$\text{NO}_3^-\text{-N}$	3.05	7.62	2.07	9.28	0.91	7.08
$\text{NO}_2^-\text{-N}$	0.61	0.48	0.38	0.99	0.4	1.56
$\text{NH}_4^+\text{-N}$	0.85	46	0.51	0.42	48	1.2
AOU	78	0.64	42	459	0.81	489
Productivity†		(0.17-1.59)§		(0.15-2.67)§		(0.11-1.34)§

*Area: A — West of $66^{\circ}30'\text{E}$; B — East of $66^{\circ}30'\text{E}$ and North of $20^{\circ}30'\text{N}$; and C — $20^{\circ}30'\text{N}$ to $17^{\circ}30'\text{N}$.

†Unit $\text{gC m}^{-3} \text{day}^{-1}$, and measured from surface to maximum 75 m.

‡Figures denote percentages of organic P in relation to total P.

§Figures are ranges of values over the areas.

The different components of nutrients help in understanding their influence on water masses more clearly than their total inorganic concentrations. Moreover, for a quantitative study of the effective nutrient flux, the fractionation can be expected to give a better picture than that of the overall nutrient transfer. Based on the ratios given in Table 1, various phosphorus fractions for the 2 layers have been calculated applying the oxidative ratio to the average values of the related variables and are presented in Fig. 10. An example of the calculations for both the layers in area (A) is presented in Table 3.

It can be seen from Table 3 that if all the phosphorus were released from the oxidation of organic matter, the oxygen saturation values to be expect-

ed would be 32 and -47% for the upper and the deeper layers respectively. This is evidently not the case, for both the layers seem to be enriched by nutrients as a result of turbulence, diffusion and other physical processes. In the upper layer, the excess of oxygen remaining after the oxidation of organic matter could be the result of the limiting quantities of phosphorus or organic matter present or it may be the effect of averaging of the values from all the stations. It is seen that in the upper layer, oxygen is available in excess, while in the deeper layers more oxygen is required, than is available, to complete the oxidation process. Similar condition is observed in the eastern tropical North Pacific also; whereas in the Atlantic oxygen is always available in large excess even

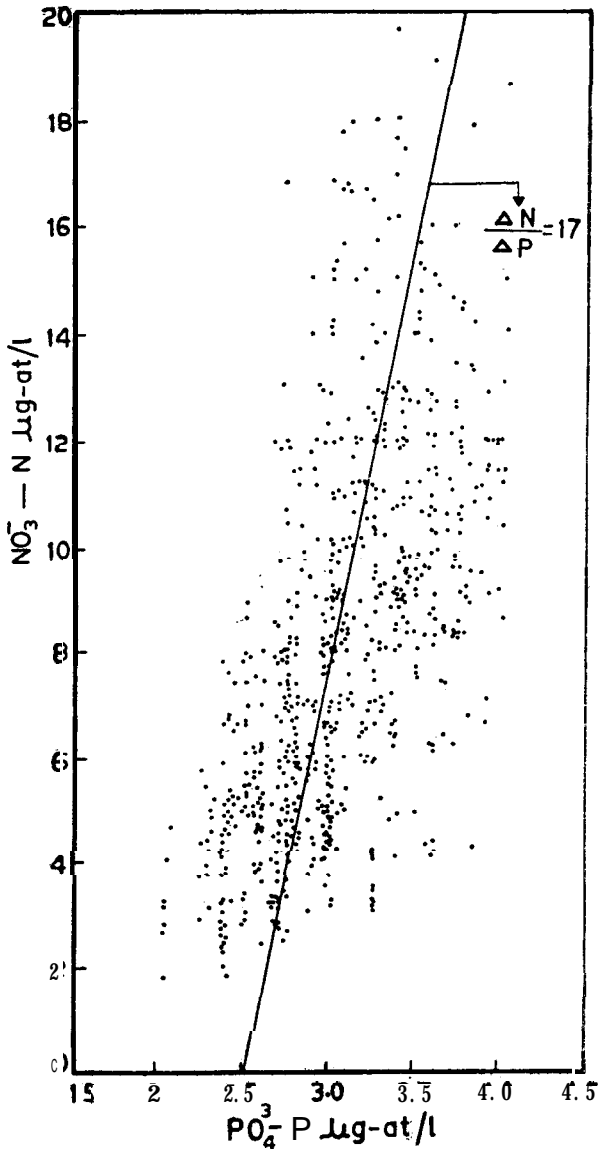


Fig. 8 — Correlation between nitrate-nitrogen and phosphate-phosphorus in the deeper layers (from 150 m to AOU maximum)

after the oxidation process had reached its completion'.

A close examination of Fig. 10 indicates that among all the areas studied total phosphorus content is the highest in the deeper waters in area (B). Reserved phosphorus has highest values in this area also. From a study of all the hydrographic observations on record it has been concluded¹ that the Arabian Sea surface water mass is formed in the north-eastern part of the basin caused by intense evaporation in this area. This watermass sinks down to a depth of about 150 m. Thermohaline convection caused by the evaporation makes the water mass almost homogeneous and this probably result in high phosphate concentration in the upper layers which causes high photosynthetic productivity. Observations during the cruises³⁶ indicate that photosynthetic productivity values in area (B) are the highest of all the areas observed (av. 0.96 gC m⁻² day⁻¹ with the range 0.15 to 2.7). It

TABLE 3 — COMPUTED RELATIONSHIPS BETWEEN OXYGEN AND PHOSPHORUS AND NITROGEN FRACTIONS IN THE 2 LAYERS IN AREA (A)

(Values expressed in pg-at/litre)

		Upper layer	Deeper layer
OXYGEN			
Oxygen saturation	O ₂	434	531
Av. oxygen CONC.	O ₂	356	71
Apparent oxygen utilization	O ₂ -O ₂	78	460
Oxygen saturation		82%	13%
PHOSPHORUS			
Inorganic	PO ₄ ³⁻ -P	1.27	2.90
Equivalent oxygen	270 x 1.10	297	
Utilization	270 x 2.90		783
P of oxidative origin	Pox = AOU/270 = AOU/270	0.29	1.70
Reserved phosphorus	Pr = PO ₄ ³⁻ - P-Pox	0.98	1.20
Excess O ₂	100% O ₂ - 270 x PO ₄ ³⁻ - P	137	
	100% O ₂ - 270 x PO ₄ ³⁻ - P		- 252
O ₂ saturation	(137/434) x 100 (-252/531) x 100	32	47 %
NITROGEN			
Nitrate	NO ₃ ⁻	3.05	7.62
Equivalent oxygen	16 x NO ₃ ⁻	49	
utilization	16 x NO ₃ ⁻		122
NO ₃ ⁻ of oxidative origin	Nor = AOU/16 = AOU/16	4.87	28.75
Reserved nitrate	Nr = NO ₃ ⁻ - Nor	-1.82	-21.13
Excess O ₂	100% O ₂ - 16 x NO ₃ ⁻ 100% O ₂ - 16 x NO ₃ ⁻	385	409
O ₂ saturation	(385/434) x 100 (409/531) x 100	89	77%

appears that even this high production is not able to consume more than 10% of the available inorganic phosphate leaving high values of P_r. These high P_r are the result of intense mixing in this area.

Intensity of oxidation of organic matter appear to be the strongest in the deeper waters of area (C), where organic phosphorus forms only 4% of total phosphorus content. This intense oxidation will result in very low concentrations of dissolved oxygen. In fact, it has been observed before (Figs. 3 and 4) that oxygen concentration in the layer between 125 m and AOU maxima is the lowest in area (C).

In the upper layers, in general, the organic fraction of phosphorus varies from 40 to 70% of the total phosphorus. This agrees well with the general conclusion that about two-thirds of phosphorus in the surface layers of the oceans is of organic origin. In the deeper layers, the organic fraction is very low and varies between 7 and 25% of the total phosphorus concentration. This, again, is in conformity with the values from deep waters in the oceans where about 90% of phosphorus has been observed to be of inorganic origin caused mostly by mineralization'.

An attempt had also been made to study the cycle of phosphorus in waters close to the bottom. Taking the average values for inorganic phosphate and apparent oxygen utilization at depths of 40 to 100 m above the bottom at all the stations deeper

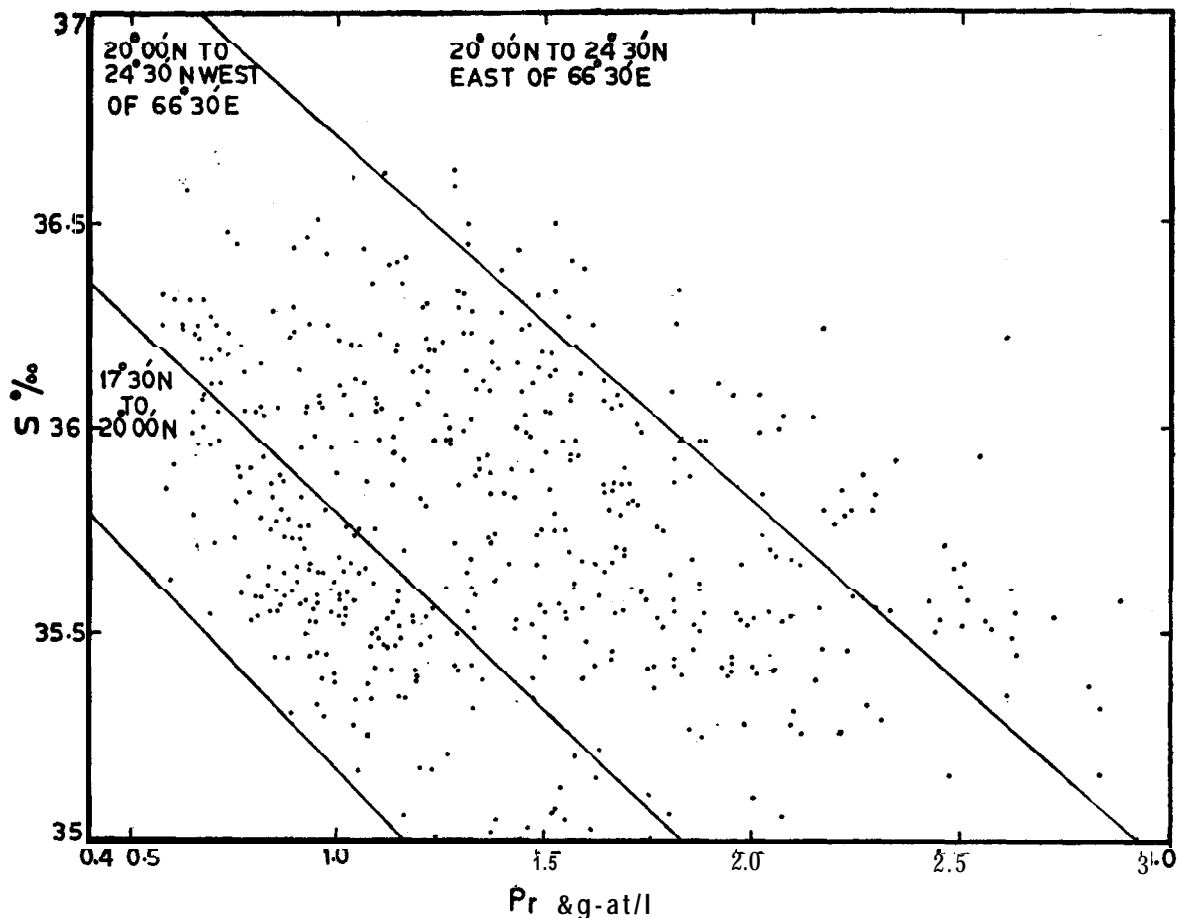


Fig. 9-Relationship between salinity and reserved phosphorus (Pr) at all the stations in the area of observation

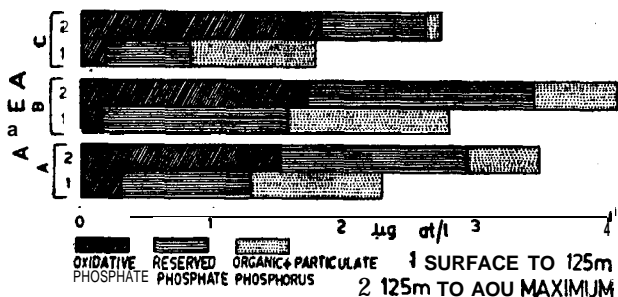


Fig. 10— Phosphorus fractions in the 2 water layers in the 3 sections studied [Calculated on the basis of the oxidative ratio in Fig. 7 and the relation outlined in Table 1]

than 1000 m we get 3.14 and 452 $\mu\text{g-at/litre}$ respectively. Applying the AAOU:AP relation of 270:1 by atoms (Fig. 7) it can be calculated that close to the bottom P_{ox} and P_r are 1.67 and 1.47 $\mu\text{g-at/litre}$ respectively. P_r in the upper layers is 1.02 $\mu\text{g-at/litre}$ on an average. This amount can only be supplied in full or in part though vertical flux from deeper waters to the surface. P_r in deeper layers is a combination of organic decomposition and the original phosphate concentrations in waters in their areas of formation. Therefore, in the deep waters 0.45 $\mu\text{g-at/litre}$ phosphorus will be left in excess. To maintain balance of phosphorus; this

amount has to be cycled through precipitation and dissolution. In the oceans there is always an excess of oxygen near the bottom⁷ and as such precipitation can be expected to be more than dissolution. It has been concluded, from this, that an amount equivalent to about 15-20% of the available inorganic phosphate in the bottom waters is removed to the sediments by inorganic processes. The process has to be inorganic since about 90% of phosphorus near the bottom in the oceans is of inorganic origin and phosphorus can only be removed from water either in apatite form or by adsorption to ferric hydroxide particles.

Nitrate Deficits (Anomalies)

Concentrations of nitrate in this region of the Arabian Sea were, in general, lower than in other regions. Average nitrite concentrations in the 2 layers of the 3 areas ranged from 0.38 to 0.61 and 0.48 to 56 $\mu\text{g-at/litre}$ respectively. There was almost always a nitrite maximum in the upper layers just below the depth of thermocline, the values of which ranged from 1.46 to 2.24 $\mu\text{g-at/litre}$. Similar features were observed in the northern Arabian Sea³⁷ and later during the IIOE by almost all research vessels engaged in chemical oceanographic observations. A secondary nitrite maximum was also observed around 300-400 m^{37,38}. In the present study a secondary nitrite maximum was

observed occasionally at around the same depth interval ranging from 2.02 to 3.22 $\mu\text{g-at/litre}$.

This raises the question concerning the amount of reduction of nitrate beyond nitrite, presumably to gaseous nitrogen, and the rates of these processes.

The amount of nitrate reduction is estimated from the following equations:

$$\delta N = (\text{NO}_3^-)_{\text{exp}} - (\text{NO}_3^-)_{\text{obs}} - (\text{NO}_2^-)_{\text{obs}} \quad \dots(1)$$

where $(\text{NO}_3^-)_{\text{exp}}$ is the amount of nitrate expected from both the oxidative and the reserved sources, which represents the concentrations expected to be present before the onset of nitrate reduction and has been calculated from the AOU nitrate and phosphate relationships established earlier. The other terms on the right hand side of Eq. (1) are observed quantities. Because of its low concentration throughout the water column ($<1 \mu\text{g-at/litre}$) except the near-surface layer, ammonia-nitrogen is not included in the calculation, assuming that the error due to this would be negligible.

The first term on the right hand side of Eq. (1) for nitrate-anomaly is:

$$(\text{NO}_3^-)_{\text{exp}} = (\text{NO}_3^-)_{\text{ox}} \pm (\text{NO}_3^-)_r \quad \dots(2)$$

where $(\text{NO}_3^-)_{\text{ox}}$ has been calculated from the relation in Table 1.

Applying Eqs. (1) and (2) attempt has been made to study the nitrate deficit in the low-

oxygenated waters of the 3 areas using the average values of nitrate and AOU (Fig. 11). Two maxima in the anomaly are observed from the values from areas A and B which coincide well with the oxygen minima. At the first maximum in the anomaly a higher value is noted in area B which might have been the result of higher quantity of organic matter in the area. It appears that the anomalies are due to low oxygen values and are not quite related to the nitrite maxima. This is evident from the values from area C where oxygen concentrations have been observed to be the lowest resulting in higher values in the nitrate anomaly.

Nitrate lost due to denitrification can now be calculated. The average of all the anomaly values comes to about 16 $\mu\text{g-at/litre}$ while the average nitrate concentration is about 8 $\mu\text{g-at/litre}$. Thus, it can be expected that on an average two-thirds of the nitrate is lost due to denitrification in the area of observations increasing in its magnitude from north to south.

Stoichiometric Relationships

Redfield⁸ observed that the ratios of change in carbon, nitrogen and phosphorus in sea water were approximately similar to the ratios of concentration of these elements in plankton, Redfield's C:N:P relation, 140:20:1 by atoms, when corrected for salt error in the analytical method for phosphorus³⁰

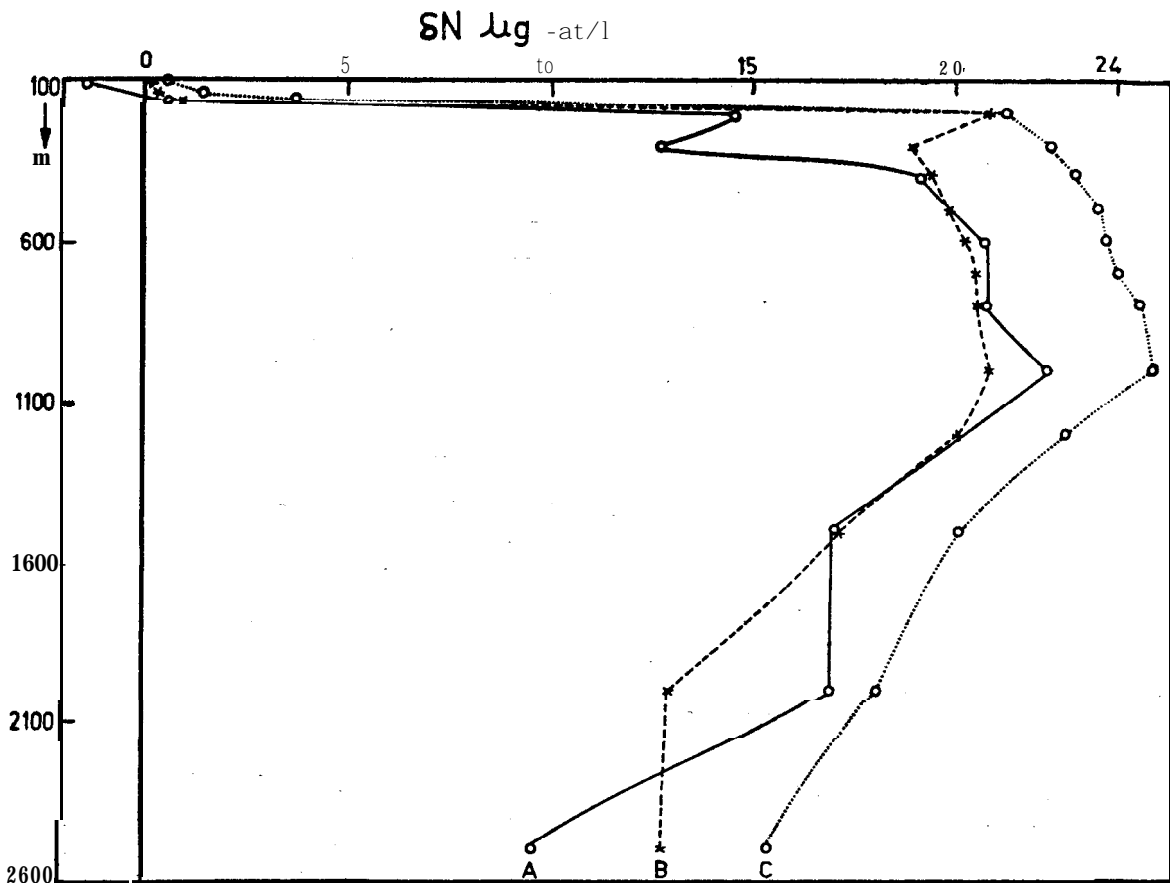


Fig. 11 — Nitrate deficiency with depth in areas A, B and C (Fig. 1 -clarification in the text) calculated from the average values applying Equation 1

and based on new observation material was finally 106:16:1 by atoms for oceanic environments@.

Because of differing marine conditions, the stoichiometric relationships cannot be the same everywhere. The ratio may not hold good in coastal regions where the proximity of land, river runoff and also the influence of local flora and fauna will change the situation. The only attempt to deduce different stages in the oxidation of organic matter and to present a stoichiometric model and to verify it in different oceanic areas has taken into consideration the inherent limitations on the subject⁹⁻¹¹. The present attempt following the lines of Richards⁹ aims at presenting a picture of conditions to be expected in the northern and the eastern basins of the Arabian Sea resulting from the oxidation of organic matter. The conclusions are based mostly on observed values with some theoretical assumptions.

Composition of organisms : A working hypothesis — Table 4 gives the result obtained from analysis of plankton, collected in the inshore waters off the Goa coast and some laboratory cultures. The average N:P ratio, combining all the values, comes to 15:1 by atoms.

It has been suggested earlier that denitrification and residual phosphate will influence the ratios in the upper layers. We have, therefore, used only the atomic relations calculated for the deep waters, which are 270:1 for ΔAOU:ΔP (Fig. 7) and 17:1 for AN:AP (Fig. 8).

It has been observed from studies in many areas with varied hydrographic conditions that though the ΔN:ΔP relation in water may vary, sometimes significantly, from the oceanic values, N:P ratio in plankton remains essentially unchanged. It is assumed that N:P ratio obtained from the analysis of plankton from the inshore region will not show significant difference from areas offshore. Further, the difference between the average values obtained in natural population and the overall average being not very significant, it has been decided to apply the latter in the present calculations.

It has been concluded before that the ratios in water may vary from place to place depending mostly on the stage of denitrification process. But assumption about the uniformity in composition of plankton organisms would, probably, indicate that the general pattern of oxidation of organic matter may not differ spatially, particularly at the first stage when only dissolved oxygen is consumed. Therefore, an attempt has been made to present a general picture of the overall process.

It is assumed that the average oxidation state of carbon is that of carbohydrate (CH₂O), the bound nitrogen is in the amino form, and the oxidation state of phosphorus is that of orthophosphate. The organic matter can thus be tentatively suggested as having the composition (CH₂O)_n(NH₃)₁₅H₃PO₄. If the organic matter is completely oxidized by oxygen and the first step in organic decomposition is the hydrolytic release of ammonia with concurrent biochemical oxidation of carbohydrate, different stages in the process can be represented by the following equations :

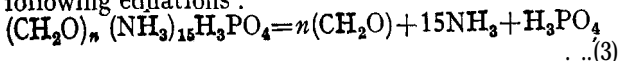


TABLE 4—ANALYSIS OF PLANKTON (NATURAL AND CULTURE)

Date	Composition	N	P	N: P ^a
NATURAL				
4 March 1975*	Mainly phyto-plankton	0.89	0.08	11: 1
	Mainly zoo-plankton	3.62	0.29	12.5: 1
17 March 1975*	Mainly phyto-plankton	2.32	0.18	12.9: 1
		1.24	0.1	12.4: 1
		1.21	0.08	15.0: 1
		2.86	0.24	11.9: 1
18 March 1975*	do	1.44	0.12	12.0: 1
		0.92	0.08	11.5: 1
		1.55	0.12	12.9: 1
24 July	do	86.25	4.51	19.9: 1
		77.50	3.93	19.7: 1
CULTURE				
July 1975†	<i>Chlorella</i> spp‡	29.63	1.93	15.3: 1
	<i>Tetraselmis</i> spp‡	37.75	1.28	29.4: 1
	<i>Tetraselmis gracilis</i> ‡	50.25	2.77	18.0: 1
Aug. 1975	<i>Artemia</i> spp (Californian strain)§	275	39.15	7.0: 1
Aug. 1975†	<i>Artemia</i> spp (Indian strain)§	45 45	2.26 2.26	19.9: 1 19.9: 1

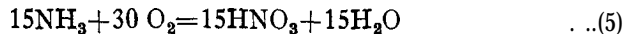
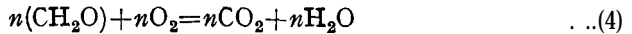
*Values in μg-at/g dry matter.

†Values in μg-at/45 ml.

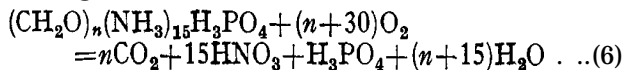
‡By courtesy of Mr V. P. Devassy.

§Dr Joseph Royan of Biological Oceanography Division, NIO.

^aN: P average for natural, 13.8 : 1; for culture, 18.2 : 1 and for all values 15.4 : 1.



Adding, the overall reaction will be



It is calculated that the atomic ratio of consumption of oxygen to phosphorus regeneration in water is 270 : 1. This would give

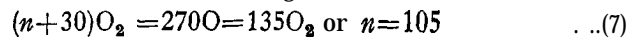


Fig. 12 shows the relation between CO₂ and oxidation equivalents. Difference between the saturation value and the titration value has been used as the apparent oxygen utilization. It has been observed⁴² that the inclusion of ammonia in the calculation of oxidation equivalents gives a better representation of the same assuming that all ammonia originates from nitrate reduction in non-anoxic or suboxic waters and nitrate as an oxidant is equivalent to 4 atoms of oxygen (NH₄⁺ + 2O₂ ⇒ NO₃⁻ + 2H⁺ + H₂O). Average concentrations of ammonia in the waters of this region varied from 0.51 to 1.22 μg-at/litre for upper layer and from 0.42 to 1.20 μg-at/litre for the deeper layer between the 3 areas. Thus it is apparent that inclusion of ammonia will not affect the calculation of the oxidation equivalents

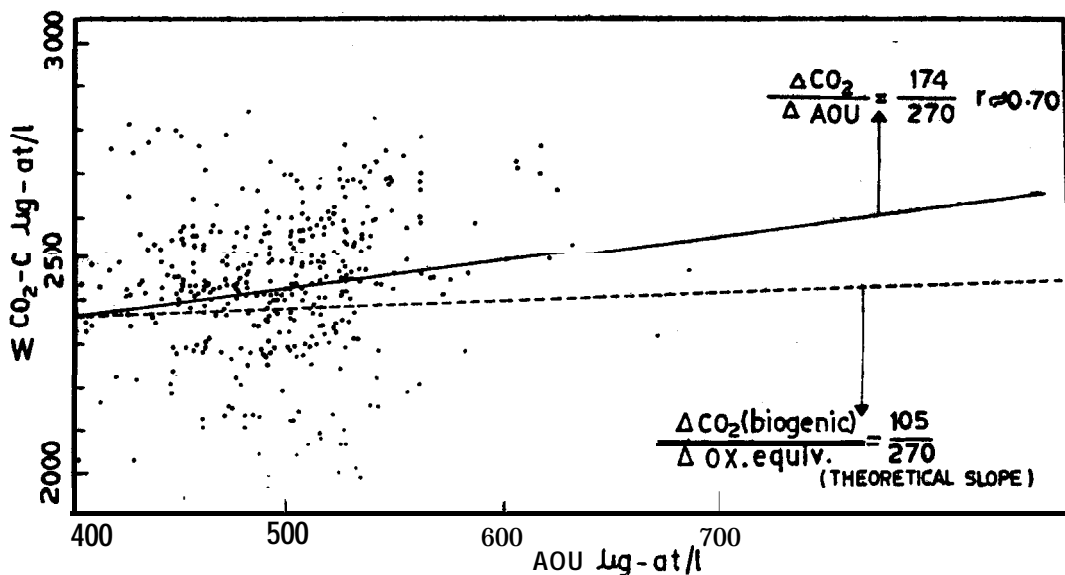


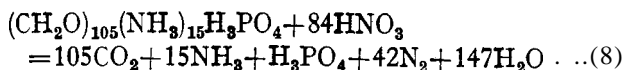
Fig. 12 — Relationship between the amount of oxygen consumed (from free oxygen only) and the total CO_2 computed from the alkalinity values in the deeper layers [Slope of the line indicates ratio between total inorganic carbon (both from the decomposition of organic matter and the possible dissolution of calcium carbonate) and oxygen consumption. Broken line is the slope for CO_2 arising from the decomposition of organic matter only (r = coefficient of correlation)]

significantly. Therefore, it is felt that leaving out of the ammonia values would not have much influence in the calculations. The total carbon dioxide values have been computed from the tables given in Strickland and Parsons²⁰ which is only a reproduction from Harvey⁴², who expanded the original work of Buch⁴³ to cover higher chlorinities—using measured values of chlorinity, temperature, pH and total alkalinity. The slope of the regression line in Fig. 12 gives a ratio between total CO_2 production and oxidation equivalents as 174/270. Ratio between biogenically produced CO_2 and oxidation equivalents, from Eq. (7) is only 105/270. The difference may simply be explained as analytical and computational error, since it is a relation between two computed quantities only. But there can be some oceanographic explanations as well. It has been observed⁴⁴ that at an intermediate depth in the ocean conditions are ideal for lime-secreting organisms to exist, which is later found to be applicable to the northern Indian Ocean including its 2 arms, the Bay of Bengal and the Arabian Sea⁴⁵. This might have influenced the ratio. Boric acid and borate ions are known to play a significant role in the regulation of alkalinity in sea water and they might have also some influence. In the absence of data from direct CO_2 analyses by gasometric methods from the Indian Ocean, this explanation may be accepted for the purpose of the present study.

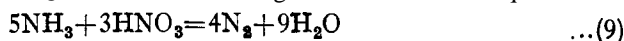
Thus the organisms in the northern and the eastern basins of the Arabian Sea appear to have an approximate composition of $(\text{CH}_2\text{O})_{105}(\text{NH}_3)_{15}\text{H}_3\text{PO}_4$. Ratio of oxygen consumption to CO_2 production becomes 2.6 in agreement with values from other oceanic areas. Therefore, in the regions studied, complete oxidation of organic matter associated with 1 atom of phosphorus would require 270 atoms of oxygen and will be accompanied by

the release into the water of 1 phosphate ion, 15 nitrate ions and 105 molecules of CO_2 .

Denitrification — When all or nearly all of the free dissolved oxygen has been consumed, nitrate ions are the next most abundant source of free energy for the oxidation of organic matter⁹. The process in which they serve as the reducible substrate is denitrification and evidence suggests that the process produces nitrite ions as intermediate and free molecular nitrogen as an end product. The limiting concentration of oxygen that can be present at the inception of denitrification is uncertain and probably depends on the nitrate concentration, but in any event it is relatively low—probably of the order of tenths of a ml/litre. Since very low concentrations of oxygen, around 0.1-0.2 ml/litre or less, have often been observed in the northern Arabian Sea associated with low nitrate and maximum of nitrite at intermediate depths it is quite possible that denitrification takes place with the loss of inorganic nitrogen compounds to gaseous nitrogen. An attempt has been made to study this process applying the stoichiometric relation deduced above. Denitrification in this basin can be represented by the equation



This reaction indicates that ammonia released during denitrification is not oxidized. However, it is very possible that it does oxidize, since the concentration of ammonia in this basin is almost insignificant, according to the basic equation



If this were so, the overall reaction would be

$$(\text{CH}_2\text{O})_{105}(\text{NH}_3)_{15}\text{H}_3\text{PO}_4 + 93\text{HNO}_3 \\ = 105\text{CO}_2 + 54\text{N}_2 + \text{H}_3\text{PO}_4 + 174\text{H}_2\text{O} \dots (10)$$

The average of the observed values of nitrate concentrations in the deeper layer is about 8 µg-at/litre. Applying Eq. (10) it is observed that about 90% of the available nitrate should be lost by denitrification. It has been suggested earlier that about two-thirds of nitrate can be lost as gaseous nitrogen. The difference may be due to analytical errors, errors in the statistical treatment or due to spatial variations in nitrate concentration. The presence of nitrite indicates that the process is incomplete in this water mass, as nitrite can appear as an intermediate product both during nitrification and denitrification ($\text{NO}_3^- \rightleftharpoons \text{NO}_2^- \rightleftharpoons \text{NH}_4^+$). It is concluded that denitrification proceeds at an intermediate depth in the northern Arabian Sea but the process does not reach its completion. A study of the dissolved gaseous nitrogen in this area will definitely help to find the 'missing link' in the chemistry of inorganic nitrogen in the Arabian Sea.

Comparison with Other Areas

The present data from the northern Arabian Sea are compared with data from the eastern North Atlantic and the eastern tropical Pacific Ocean. Calculations for nutrient fractions from the unpublished data collected on board *RRS Discovery* during its cruise in June-July 1967 along a section extending from the Faro Bank Channel in the north to the Bay of Biscay in the south in the eastern North Atlantic by one of the authors (R.S.G.) are presented in Table 5.

The calculations show that oxidative phosphorus and nitrogen forms a minor portion of the total concentrations of their inorganic forms. Being an area which is well ventilated the oxygen concentration never goes below 4 ml/litre which does not give a significant apparent oxygen utilization value.

In contrast, in the northern Arabian Sea oxidative phosphorus forms a major part of the total inorganic phosphate while oxidative nitrogen is much higher than the inorganic nitrogen present in water. This difference results in negative values of the reserved fraction.

LGW oxygen concentration gives a high apparent oxygen utilization value. It appears that because of denitrification the supply of nitrogenous organic matter may not be sufficient or the low oxygen content of the water inhibits the regeneration process and organic matter settles undissociated. But values of organic phosphorus seem to be quite comparable with general oceanic condition where inorganic phosphates make up for about 90-95% of total phosphorus concentration in deep water. Therefore, it appears that insufficient supply of organic matter is the cause of deficiency of inorganic nitrogen compounds in the Arabian Sea. This may also be caused by poor mixing of oxygen-rich bottom water with intermediate water masses causing the secondary oxygen minimum to appear. This minimum may also be the effect of the minimum in the equatorial Indian Ocean. There it appears at around 1000 m and has an oxygen concentration of about 1.5 ml/litre. This water mass seems to spread northwards and the oxygen concentration is depleted with its northerly transport due to the oxidation of organic matter resulting from the productivity in the euphotic layers of the regions of its passage.

Appearance of oxygen minimum and nitrite maximum at intermediate depths, the cause of which has been attributed to denitrification, has also been observed in the eastern tropical North Pacific^{46,47} and in waters off the coast of Peru^{48,49}. Considering the hydrographic conditions in the Arabian Sea and the Bay of Bengal and comparing then similarities with the eastern tropical North Pacific Ocean it may be concluded that these are characteristics of oceanic areas, not well ventilated in the north and lying off the western coasts of continents. These are generally the areas of intense upwelling and the resultant high photosynthetic productivity seem to be a major cause for these phenomena. The Atlantic is well ventilated both in the north and in the south and that is why neither any oxygen minimum nor any nitrite maximum could be observed along the western shores of the continents bordering it.

It is concluded that the normal oceanic C:N:P relation of 106:16:1 by atoms is also maintained in the Arabian Sea by the normal mechanism in its deep water and by somewhat different mechanisms in its upper layers, which can be compared to conditions in oxygen-poor semi-enclosed quasi-oceanic or brackish water basins considerably influenced by river runoff where the relation is also maintained but by very different mechanisms^{15,16}.

Complications and Limitations

In calculating the ratios of change by the least square method, it was assumed that the variables are linearly related. This assumption is uncertain and the regression lines may not always be the ideal fit through the points. Also, components

TABLE 5 — COMPUTED RELATIONSHIPS BETWEEN OXYGEN, PHOSPHORUS AND NITROGEN FRACTIONS BELOW 75 m IN THE EASTERN NORTH ATLANTIC BASED ON ATOMIC RELATIONS AAOU: AP = 286: 1 AND AAOU: AN = 22 : 1

(Units are in µg-at/litre)

OXYGEN		
Oxygen saturation (from O ₂ t°C and S‰)		606
Av. oxygen conc.	O ₂	520
Apparent oxygen utilization O ₂ -O ₁		86
Oxygen saturation		86%
PHOSPHORUS		
Inorganic	PO ₄ ³⁻ P	0.99
Equivalent oxygen utilization	286 X PO ₄ ³⁻ P	283
P of oxidative origin	P _{ox} = AOU/286	0.30
Reserved phosphorus	P _r = PO ₄ ³⁻ P - P _{ox}	0.69
Excess O ₂	100% O ₂ - 286 X PO ₄ ³⁻ P	323
Oxygen saturation	(323/606) X 100	53%
NITROGEN		
Nitrate	NO ₃ ⁻	10.18
Equivalent oxygen utilization	22 X NO ₃ ⁻	224
NO ₃ ⁻ of oxidative origin	N _{or} = AOU/22	3.91
Reserved nitrate	N _r = NO ₃ ⁻ - N _{ox}	6.27
Excess O ₂	100% O ₂ - 22 X NO ₃ ⁻	382
Oxygen saturation	(382/606) X 100	63%

for which oxidation equivalents were sought were assumed to be invariant. The reverse would, probably, result in somewhat different relations. Tests have however, shown that the difference with the reverse relations lie within the limits of errors in the analytical and statistical methods.

The stoichiometric model has been suggested from measurements on one occasion each year for 2 yrs at only a few stations in a fjord-like area with permanently anoxic conditions at the bottom¹⁰. Agreement, calculated from observations from closely spaced stations over a wide oceanic area with near-anoxic or sub-oxic conditions at intermediate depths, suggests the universal validity of the model in the oceans.

The possible chemical complication have been reviewed by Richards⁹. The analytical methods are also bound to influence the results and the ultimate conclusions. The measurements are carried out by different analysts and the errors due to personal bias in them cannot be uniform.

In spite of all these complications and limitations it may be concluded that the relationships suggested here would probably give an approximate idea of the overall conditions which can be expected from the decomposition of organic matter in the northern and the eastern basins of the Arabian Sea. Also, because of the similarity of the ratio with those prevailing in other oceanic areas the relationship, suggested here, can be expected to be valid for the Indian Ocean as a whole.

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